

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
 United States Patent and Trademark
 Office
 Box PCT
 Washington, D.C. 20231
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 25 May 2000 (25.05.00)	
International application No. PCT/NO99/00280	Applicant's or agent's file reference 101528tfm
International filing date (day/month/year) 14 September 1999 (14.09.99)	Priority date (day/month/year) 16 September 1998 (16.09.98)
Applicant OLSVIK, Ola et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

11 April 2000 (11.04.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer C. Villet
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

BRYN & AARFLOT AS

14 APR. 2000

PCT

NOTICE INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

BRYN & AARFLOT AS
P.O. Box 449 Sentrum
N-0104 Oslo
NORVÈGE

Date of mailing (day/month/year)

06 April 2000 (06.04.00)

Applicant's or agent's file reference

101528tfm

IMPORTANT NOTICE

International application No.

PCT/NO99/00280

International filing date (day/month/year)

14 September 1999 (14.09.99)

Priority date (day/month/year)

16 September 1998 (16.09.98)

Applicant

DEN NORSKE STATS OLJESELSKAP A.S et al

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
- AU,CN,JP,KP,KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AE,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CR,CU,CZ,DE,DK,DM,EA,EE,EP,ES,FI,GB,GD,GE,
GH,GM,HR,HU,ID,IL,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MD,MG,MK,MN,MW,MX,NO,NZ,OA,
PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 06 April 2000 (06.04.00) under No. WO 00/18680

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

J. Zahra

Telephone No. (41-22) 338.83.38

Form PCT/IB/308 (July 1996)

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7. MAR. 2001 10:53

BRVA & AARFLOT AS +47 22003131

NO. 399

P. 3
WO 00/18680
PCT/NO99/00280

Continuation of Form PCT/IB/308

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF
THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

Date of mailing (day/month/year) 06 April 2000 (06.04.00)	IMPORTANT NOTICE
Applicant's or agent's file reference 101528tfm	International application No. PCT/NO99/00280
<p>The applicant is hereby notified that, at the time of establishment of this Notice, the time limit under Rule 46.1 for making amendments under Article 19 has not yet expired and the International Bureau had received neither such amendments nor a declaration that the applicant does not wish to make amendments.</p>	

PATENT COOPERATION TREATY

PCT

REC'D 13 DEC 2000

WIPO PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

15

Applicant's or agent's file reference 101528TFM	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NO99/00280	International filing date (day/month/year) 14/09/1999	Priority date (day/month/year) 16/09/1998
International Patent Classification (IPC) or national classification and IPC C01B3/32		
Applicant DEN NORSKE STATS OLJESELSKAP A.S. et al.		



- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 6 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of sheets.

- This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 11/04/2000	Date of completion of this report 11.12.00
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Van Iddekinge, R Telephone No. +49 89 2399 8346 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NO99/00280

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

Description, pages:

1-15 as published

Claims, No.:

1-20 as published

Drawings, sheets:

1,2 as published

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NO99/00280

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application.

☒ claims Nos. 17-20.

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☒ no international search report has been established for the said claims Nos. 17-20.

2. A meaningful international preliminary examination report cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the standard.

☐ the computer readable form has not been furnished or does not comply with the standard.

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)

Yes: Claims 3,4,6,8-14,16

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NO99/00280

	No:	Claims	1,2,5,7,15
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-16
Industrial applicability (IA)	Yes:	Claims	1.16
	No:	Claims	

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NO99/00280

Re Item III

Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

- 1). An international search report has been made for claims 1-16. Claims 17-20 have not been searched, because of lack of unity. Therefore no substantive examination is possible for claims 17-20.

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

- 2). Reference is made to the following documents:
D1=US-A-5714132
D2=US-A-4699772
D3=EP-A-289419

Novelty

- 3). D1 discloses a process for producing a CO₂ rich gas and a H₂ rich gas according to claim 1 of the application, see D1: claims 1-4, 18, 19; figure 3; column 5, lines 22- 54; column 7, lines 50-column 8, line 18; example II; Table II.

D1 also discloses the additional features of dependent claims 2, 5, 7, 15.

Therefore claims 1 and its dependent claims 2, 5, 7, 15 do not fulfil the requirements of Article 33(2) PCT (novelty).

The additional features of dependent claims 3, 4, 6, 8-14, 16 do not appear, in combination with the features of any claim to which they refer, to involve an inventive step.

Therefore dependent claims 3, 4, 6, 8-14, 16 of the application do not fulfil the requirements of Article 33(3) PCT (inventive step).

Re Item VII

Certain defects in the international application

- 4). Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the document D1 is not mentioned in the description, nor is this document identified therein.

Re Item VIII

Certain observations on the international application

- 5). The term "carbon part" used in claims 7, 8 is vague and unclear and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claims unclear (Article 6 PCT).
- 6). The embodiment of the invention described in claim 11 does not fall within the scope of claim 1 (a partial oxidation reactor is not a reforming reactor). This inconsistency between the claims leads to doubt concerning the matter for which protection is sought, thereby rendering the claims unclear (Article 6 PCT).

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ :

C01B 3/32, 31/20

A1

(11) International Publication Number:

WO 00/18680

(43) International Publication Date:

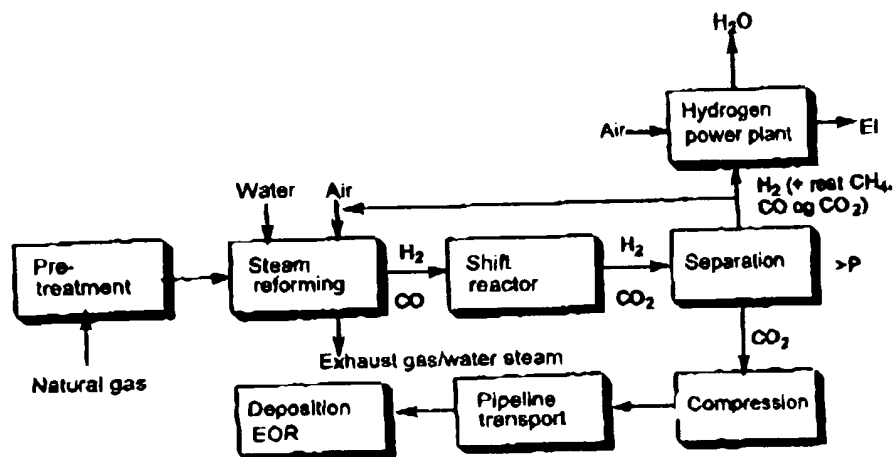
6 April 2000 (06.04.00)

(21) International Application Number: PCT/NO99/00280

(22) International Filing Date: 14 September 1999 (14.09.99)

(30) Priority Data:
19984295 16 September 1998 (16.09.98) NO(71) Applicant (for all designated States except US): DEN NORSKE
STATS OLJESELSKAP A.S [NO/NO]; N-4035 Stavanger
(NO).

(72) Inventors; and

(75) Inventors/Applicants (for US only): OLSVIK, Ola [NO/NO];
Haukv. 18, N-7562 Hundhammeren (NO). HANSEN,
Roger [NO/NO]; Sildræp. 70B, N-7048 Trondheim
(NO). GRISLINGÅS, Arne [NO/NO]; Ole Nordgaardsvei
36B, N-7049 Trondheim (NO). RYTTER, Erling [NO/NO];
Steinåsen 19, N-7049 Trondheim (NO).(74) Agent: BRYN & AARFLOT AS; P.O. Box 449 Sentrum,
N-0104 Oslo (NO).(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG,
BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE,
ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP,
KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD,
MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD,
SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US,
UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS,
MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ,
BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GW, ML, MR, NE, SN, TD, TG).**Published***With international search report.**Before the expiration of the time limit for amending the
claims and to be republished in the event of the receipt of
amendments.**In English translation (filed in Norwegian).*(54) Title: PROCESS FOR PREPARING A H₂-RICH GAS AND A CO₂-RICH GAS AT HIGH PRESSURE

shows known technique in the form of steam reforming with hydrogen firing

(57) Abstract

The present invention comprises a method for production of a CO₂-rich gas stream and a H₂-rich gas stream, the method comprising the following steps: a) natural gas and water are fed to a reforming reactor and are converted to synthesis gas under supply of a O₂-containing gas; b) the gas stream from a) is shifted, whereby the content of CO is reduced and the amounts of CO₂ and H₂ are increased by reaction of H₂O; c) the gas stream from b) is separated in a separation unit into a CO₂-rich and a H₂-rich gas stream, respectively. The invention also concerns the use of a CO₂-rich gas stream for injection into marine formations, and the use of a H₂-rich gas stream for hydrogenation, as a source of energy/fuel in fuel cells or for production of electricity.

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

BRYN & AARFLOT AS
P.O. Box 449
Sentrum
N-0104 Oslo
NORVEGE

BRYN & AARFLOT AS

14/09/1999

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year)

11 12 00

Applicant's or agent's file reference
101528TFM

IMPORTANT NOTIFICATION

International application No.
PCT/NO99/00280

International filing date (day/month/year)
14/09/1999

Priority date (day/month/year)
16/09/1988

Applicant

DEN NORSKE STATS OLJESELSKAP A.S. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer

Gregoire, J-P

Tel +49 89 2399-8041




PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 101528TFM		FOR FURTHER ACTION		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/NO99/00280		International filing date (day/month/year) 14/09/1999		Priority date (day/month/year) 16/09/1998
International Patent Classification (IPC) or national classification and IPC C01B3/32				
Applicant DEN NORSKE STATS OLJESELSKAP A.S. et al.				
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>				
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input checked="" type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input checked="" type="checkbox"/> Certain defects in the international application VIII <input checked="" type="checkbox"/> Certain observations on the international application 				
Date of submission of the demand 11/04/2000		Date of completion of this report 11.12.00		
Name and mailing address of the International preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx 523656 epmu d Fax +49 89 2399 - 4465		Authorized officer Van Iddekinge, R Telephone No. +49 89 2399 8346		

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NO99/00280

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*

Description, pages:

1-15 as published

Claims, No.:

1-20 as published

Drawings, sheets:

1,2 as published

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NO99/00280

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

- ☐ the entire international application.
☒ claims Nos. 17-20.

because:

- ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):
- ☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):
- ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.
- ☒ no international search report has been established for the said claims Nos. 17-20.

2. A meaningful international preliminary examination report cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

- ☐ the written form has not been furnished or does not comply with the standard.
☐ the computer readable form has not been furnished or does not comply with the standard.

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. Statement**

Novelty (N)

Yes: Claims 3,4,6,8-14,16

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NO99/00280

	No:	Claims	1,2,5,7,15
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-16
Industrial applicability (IA)	Yes:	Claims	1.16
	No:	Claims	

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NO99/00280

Re Item III**Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

- 1). An international search report has been made for claims 1-16. Claims 17-20 have not been searched, because of lack of unity. Therefore no substantive examination is possible for claims 17-20.

Re Item V**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

- 2). Reference is made to the following documents:
D1=US-A-5714132
D2=US-A-4699772
D3=EP-A-289419

Novelty

- 3). D1 discloses a process for producing a CO₂ rich gas and a H₂ rich gas according to claim 1 of the application, see D1: claims 1-4, 18, 19; figure 3; column 5, lines 22- 54; column 7, lines 50-column 8, line 18; example II; Table II.

D1 also discloses the additional features of dependent claims 2, 5, 7, 15.

Therefore claims 1 and its dependent claims 2, 5, 7, 15 do not fulfil the requirements of Article 33(2) PCT (novelty).

The additional features of dependent claims 3, 4, 6, 8-14, 16 do not appear, in combination with the features of any claim to which they refer, to involve an inventive step.

Therefore dependent claims 3, 4, 6, 8-14, 16 of the application do not fulfil the requirements of Article 33(3) PCT (inventive step).

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NO99/00280

Re Item VII**Certain defects in the international application**

- 4). Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the document D1 is not mentioned in the description, nor is this document identified therein.

Re Item VIII**Certain observations on the international application**

- 5). The term "carbon part" used in claims 7, 8 is vague and unclear and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claims unclear (Article 6 PCT).
- 6). The embodiment of the invention described in claim 11 does not fall within the scope of claim 1 (a partial oxidation reactor is not a reforming reactor). This inconsistency between the claims leads to doubt concerning the matter for which protection is sought, thereby rendering the claims unclear (Article 6 PCT).

1999-09-14

T - 1 114011/00280

18.6805


RECORD COPY

1/5

PCT REQUEST

101528tfm

Original (for SUBMISSION) - printed on 14.09.1999 09:37:15 AM

0 0-1	For receiving Office use only International Application No.	PCT/NO 99 / 00280
0-2	International Filing Date	14 SEPT. 1999 (14.09.99)
0-3	Name of receiving Office and "PCT International Application"	 PATENTSTYRET Styret for det industrielle rettssystem ► PCT International application
0-4 0-4-1	Form - PCT/RO/101 PCT Request Prepared using	PCT-EASY Version 2.84 (updated 01.06.1999)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	Norwegian Patent Office (RO/NO)
0-7	Applicant's or agent's file reference	101528tfm
I	Title of invention	PROCESS FOR PREPARING A H ₂ -RICH GAS AND A CO ₂ -RICH GAS BY HIGH PRESSURE.
II	Applicant	
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III-2	Applicant and/or inventor	
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	The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
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V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	<p>AP: GH GM KE LS MW SD SL SZ UG ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT</p> <p>EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT</p> <p>EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT</p> <p>OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT</p>
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	<p>AE AL AM AT AU AZ BA BB BG BR BY CA CH&LI CN CR CU CZ DE DK DM EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MD MG MK MN MW MX NO NZ PL PT RO RU SD SE SG SI SK SL TJ TM TR TT UA UG US UZ VN YU ZA ZW</p>
V-3	National Patent (States which have become party to the PCT after the issuance of this version of EASY)	TZ
V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.	
V-6	Exclusion(s) from precautionary designations	NONE
VI-1	Priority claim of earlier national application	
VI-1-1	Filing date	16 September 1998 (16.09.1998)
VI-1-2	Number	1998 4295
VI-1-3	Country	NO

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VI-2	Priority document request The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s):	VI-1	
VII-1	International Searching Authority Chosen	Swedish Patent Office (ISA/SE)	
VII-2	Request to use results of earlier search; reference to that search		
VII-2-1	Date	08 June 1999 (08.06.1999)	
VII-2-2	Number	1998 4295	
VII-2-3	Country (or regional Office)	NO	
VIII	Check list	number of sheets	electronic file(s) attached
VIII-1	Request	5	-
VIII-2	Description	17	-
VIII-3	Claims	3	-
VIII-4	Abstract	1	101528abs.txt
VIII-5	Drawings	2	-
VIII-7	TOTAL	28	
	Accompanying items	paper document(s) attached	electronic file(s) attached
VIII-8	Fee calculation sheet	✓	-
VIII-16	PCT-EASY diskette	-	diskette
VIII-17	Other (specified):	Copy of Official Action	-
VIII-18	Figure of the drawings which should accompany the abstract		
VIII-19	Language of filing of the international application	Norwegian	
IX-1	Signature of applicant or agent		
IX-1-1	Name	BRYN & AARFLOT AS	
IX-1-2	Name of signatory	MARKUSSEN, Tone Furan	
IX-1-3	Capacity	Patent Attorney <i>Tone Furan Markussen</i>	

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10-1	Date of actual receipt of the purported international application	14 SEPT. 1999 (14.09.99)
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	Received
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/SE
10-6	Transmittal of search copy delayed until search fee is paid	

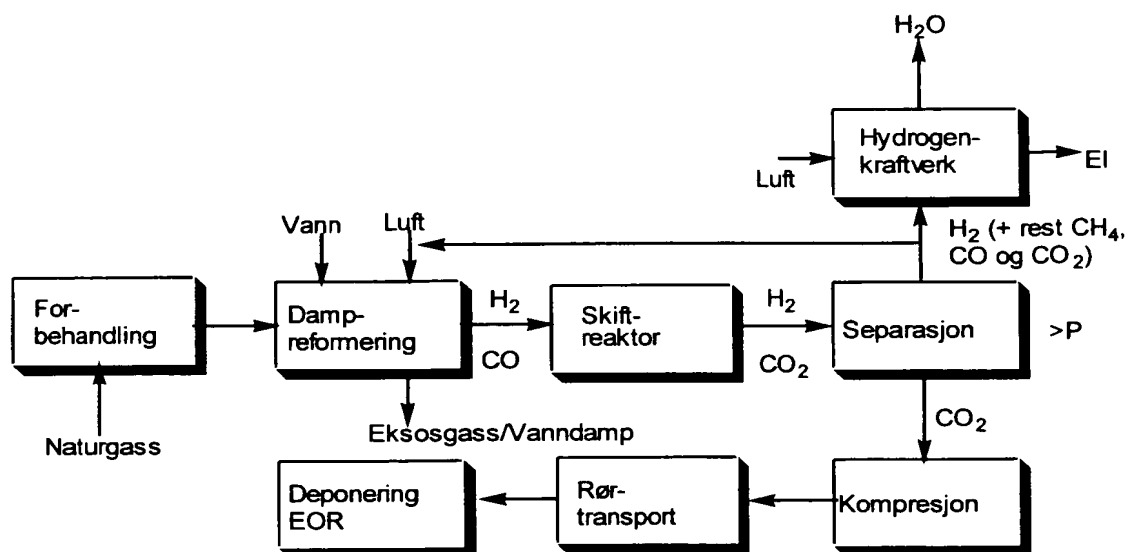
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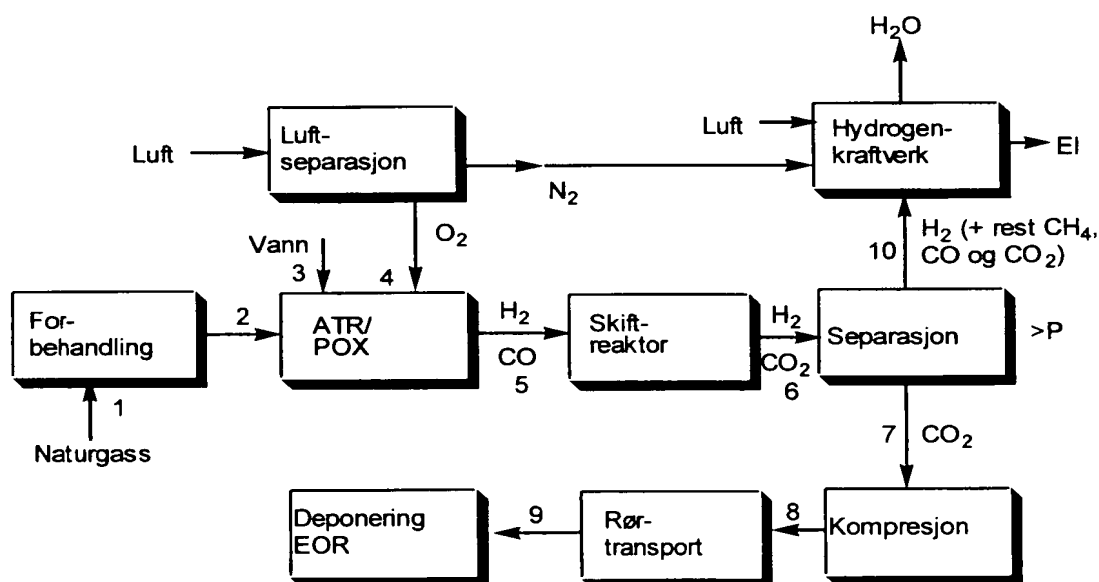
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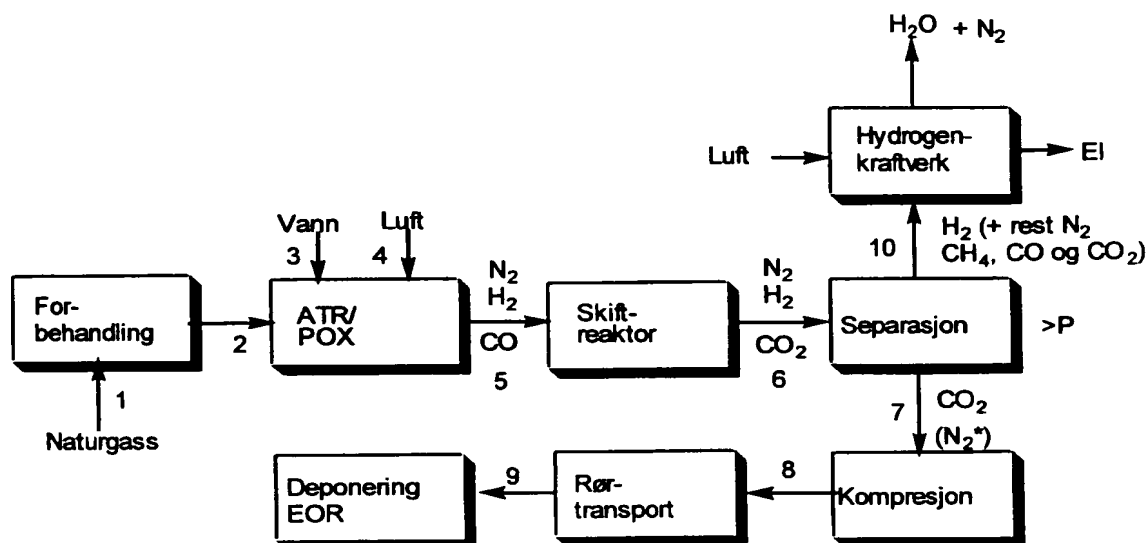
11-1	Date of receipt of the record copy by the International Bureau	05 OCTOBER 1999	(05.10.99)
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Figur 1 viser kjent teknikk i form av dampreforming med hydrogenfyring.



Figur 2 viser POX eller ATR med oksygen



Figur 3 viser POX eller ATR med luft

(N_2^*): Ved bruk av en eller flere membranenheter kjøres N_2 sammen med CO_2 .

O.nr.101528

Fremgangsmåte for å fremstille en H_2 -rik gass og en CO_2 -rik gass ved høyt trykk.

Foreliggende oppfinnelse omfatter en fremgangsmåte for fremstilling av en CO_2 -rik gass til injeksjonsformål eller deponering og en hydrogenrik gass for produksjon av energi. Videre omhandler oppfinnelsen anvendelse av henholdsvis CO_2 -rik og H_2 -rik gass.

Det er alminnelig antatt at drivhuseffekten og klimaet på jorden har en nær sammenheng med menneskeskapt CO_2 -utslipp. Dette utslippet dannes først og fremst ved forbrenning av kull og hydrokarboner, bl.a. ved generering av varme og elektrisk kraft. Et ønskelig mål er derfor å redusere utslippet av CO_2 til atmosfæren.

Det er tidligere kjent å redusere utslippet av CO_2 ved forbrenning av naturgass f.eks. ved gassreformerings- og skiftteknologi for fremstilling av en blanding bestående av hydrogen og karbondioksid. Videre separeres disse komponentene, hvorefter hydrogen anvendes som brennstoff i en gassturbin og karbondioksid deponeres etter komprimering til ønsket trykk. Deponeringen kan finne sted på havbunnen eller i geologiske reservoarer. Reservoarene kan også inneholde hydrokarboner. Ovennevnte teknikk er bl.a. omtalt i Tekniks Ukeblad nr. 16, s. 8, 1998.

Kjent teknikk omfattende gassreformerings- og skiftteknologi som beskrevet ovenfor er særdeles kostbar og gir samtidig mindre energiutbytte enn et konvensjonelt, men moderne, gasskraftverk.

US 3,652,454 beskriver fremstilling av CO_2 og H_2 fra en CO -inneholdende gassstrøm ved en forbedret kontinuerlig katalytisk skift reaksjon ved høyt trykk. Reaksjonen finner sted i en eller flere skift-reaktorer ved et superatmosfærisk trykk på fra 35-250 atm. og en temperatur på mellom $287^{\circ}C$ – $537^{\circ}C$. Patentskriftet beskriver ikke reformering av naturgass.

Fra EP 0 000 993-A1 er det kjent en fremgangsmåte for å fremstille ammoniakk ved en primær og en sekundær katalytisk reformering av en hydrokarbonstrøm ved superatmosfærisk trykk. Fra den primære katalytiske reformeringen er forholdet av damp til karbon fra 2,5-3,5, trykket er fra 30 – 120 bar og temperaturen ut
5 av reaktoren er fra 750-850°C. Fra den sekundære katalytiske reformeringen er innholdet av metan fra 0,2 – 10 vekt% på tørr basis og forholdet av hydrogen til nitrogen er fra 2,2 – 2,7. Den sekundære reformeringen tilsettes et overskudd av luft for fremstilling av en gass med et høyere innhold av metan, dvs. ved en lavere
10 temperatur, og/eller et lavere dampforhold og/eller et høyere trykk. I det ovennevnte EP patentet fjernes CO₂ ved at hydrogen tas ut ved forhøyet trykk for videre anvendelse ved fremstilling av ammoniakk.

EP 0 289 419 beskriver katalytisk dampreforming av hydrokarboner for fremstilling av hydrogen i en ammoniakkprosess. Den katalytiske dampreforming finner sted ved et trykk fra 25 – 120 bar, en temperatur fra 800-1000°C og ved et forhold av damp:karbon på 1,8-2,5. Prosessen drives slik at det er mindre enn 0,3% forurensninger i den H₂-rike gassen som skal benyttes til ammoniakkproduksjon. Foreliggende oppfinnelse tillater et høyere innhold enn 0,3% av CO, CO₂ og
20 CH₄ i den H₂-rike gasstrømmen.

CA 868,821 beskriver fremstilling av syntesegass ved dampreforming av hydrokarboner i en gass og væske ved 50-250 abs. atm., fortrinnsvis 160 abs. atm. for produksjon av ammoniakk og metanol.

25 Kjent teknikk omtaler ikke et forenklet anlegg slik som omfattet av foreliggende oppfinnelse hvor naturgass reformeres ved høyt trykk i en autoterm reformer etterfulgt av en skift-reaktor, hvoretter det frembringes en CO₂-rik gass ved et trykk i intervallet fra 1 til 100 bar noe som medfører reduserte kompresjonskostnader ved deponering og reinjisering. Det forenklede anlegget fører til at en begrenset del
30 av karbonet i råstoffet befinner seg i form av metan eller karbonmonoksid når den hydrogenrike gassblandingen fødes som brennstoff til et gasskraftverk. Et resultat

av det reduserte kravet til produktgassenes renhet medfører at ett eller flere av prosessstrinnene kan drives ved et høyere trykk, lavere temperatur og/eller lavere forhold av damp/karbon.

Foreliggende oppfinnelse tilveiebringer en fremgangsmåte for fremstilling av en CO₂-rik gasstrøm og en H₂-rik gasstrøm, hvor fremgangsmåten er kjennetegnet ved følgende trinn:

- a) naturgass og vann fødes til en reformeringsreaktor og omdannes til syntesegass under tilførsel av en O₂-holdig gass;
- b) gasstrømmen fra a) skiftes, hvor innholdet av CO reduseres og mengden av CO₂ og H₂ økes ved omsetning av H₂O;
- c) gasstrømmen fra b) separeres i en separasjonsenhet i henholdsvis en CO₂-rik og en H₂-rik gasstrøm.

Videre er det et formål ved foreliggende oppfinnelse at skiftprosessen i b) utføres i ett trinn hvor forholdet av H₂O:CO i skiftprosessen kan være fra 1 til 9, fortrinnsvis 1,5 til 4. I foreliggende oppfinnelse er trykket i den CO₂-rike gasstrømmen etter separasjonsenheten fra 1 til 100 bar, fortrinnsvis fra 5 til 50 bar. Karbonandel i den H₂-rike gasstrømmen er fra 1 til 20 volum%, fortrinnsvis fra 5 til 15 volum%. Oppfinnelsen er kjennetegnet ved at naturgassen i trinn a) tilføres en oksygenrik gass eller luft/oksygenanriket luftstrøm. Reformeringsreaktoren ifølge oppfinnelsen er fortrinnsvis en partiell oksidasjonsreaktor, særlig er en autoterm reformer. Gasstrømmen fra et forbrenningskammer i en autoterm reformer bringes i kontakt med et katalysatorsjikt. Når reformeringen finner sted i en partiell oksidasjonsreaktor utføres reaksjonen uten katalysator. Videre har gasstrømmen ut fra reformeren en temperatur i intervallet fra 800 til 1200°C. Når naturgassen i trinn a) tilføres luft/oksygenanriket luft følger minst en andel N₂ den CO₂-rike gasstrømmen igjennom prosessen. Foreliggende oppfinnelse omfatter også anvendelse av en CO₂-rik gasstrøm fremstilt ifølge den tidligere omtalte fremgangsmåten for injeksjon i marine formasjoner. Videre omfatter oppfinnelsen anvendelse av en H₂-rik gasstrøm fremstilt ifølge oppfinnelsen hvor den H₂-rik gasstrømmen kan nyttiggjøres ved hydrogenering, i elektrisitetsproduksjon og som energikilde/drivstoff i brenselceller.

Et vesentlig moment ved oppfinnelsen er at den CO_2 -rike strømmen foreligger ved et forhøyet trykk, slik at kompresjonsarbeidet som er nødvendig for å bringe trykket opp til injeksjons- eller deponerings-trykket (50-250 bar) blir så lite som mulig. Dette krever et høyt trykk gjennom alle enhetene (reformer, skiftenhet og separatorenhet). Eksempelvis kan naturgassen som fødes inn i reformeren ha et trykk på 30 -200 bar. Ved marginale trykkfall i reformeren og skiftenheten, vil trykket inn på separasjonsenheten være i samme intervall.

Foreliggende oppfinnelse gir en rekke fordeler ved fremstilling av en henholdsvis H_2 -rik og en CO_2 -rik gass. En av fordelene er at øket trykk gir økt omsetning pr. volumenhet i reformer og skift-reaktor, og videre et redusert kompresjonsarbeide av CO_2 ved en eventuell reinjisering eller deponering. Dessuten gir økt trykk redusert kompresjonsarbeide for føde til gassturbin. I reformeren er det høy primærdannelse av CO_2 som følge av høyt trykk. En annen fordel ved foreliggende oppfinnelse er en forenklet design og drift av eventuelt en gassturbin for forbrenning av den H_2 -rike gasstrømmen som følge av et visst slipp av CH_4 i reformer, CO i skift-reaktoren og CO_2 i separasjonstrinnet. Anvendelse av luft eller oksygenanriket luft ved en autoterm reformer (ATR) og partiell oksidasjon (POX) sparer oksygenanlegg og gir forenklet design og drift av ATR og gassturbin. Et visst CO-slipp dvs. uomsatt gasskomponent, unødiggjør lav-temperatur-skift og metanisering. I foreliggende oppfinnelse kan det være påkrevet med tilførsel av damp til skift-reaktoren. Et visst CO_2 slipp i foreliggende oppfinnelse forenkler separasjonsprosessen. Foregår separasjonen ved aminvask kan man kanskje klare seg med moderat trykkavlastning.

25

Foreliggende oppfinnelse omfatter en rekke utførelsesformer hvor bl.a. naturgass renses og forbehandles på en hensiktsmessig måte slik at gassføden i hovedsak vil bestå av metan etter behandling. Reformeringen foregår ved et trykk i intervallet 30 til 200 bar. Det er foretrukket å anvende en skift-reaktor ved utførelse av foreliggende oppfinnelse. Vanndamp kan tilføres skift-reaktoren, men den kan også drives uten tilførsel av vanndamp. Ved utløpet av skift-reaktoren er det godtagbart med et innhold på karbonbasis av CO på opptil 2 volum% , fortinnssvis 5 vo-

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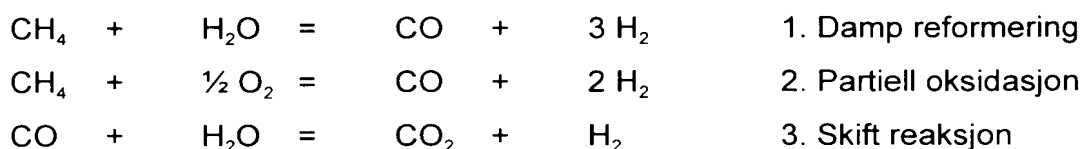
lum%, og av metan på 2 volum% , fortinnsvis 5 volum%. Videre kan den H₂-rike gasstrømmen ifølge oppfinnelsen inneholde minst 1 volum% og opptil maksimalt 20 volum% av den opprinnelige karbonmengden i naturgassen. Dampreformerer kan fyres med den hydrogenrike fyrgassen. Dersom autotermisk reformering benyttes kan minst en andel av den hydrogenrike strømmen benyttes til forvarming av fødegassen. Forvarming av fødegassen kan også utføres ved varmeveksling med varm gass fra en gassturbin.

Formålet ved foreliggende oppfinnelse er at et begrenset del av karbon i fødestrømmen/råstoffet befinner seg i form av metan, karbonmonoksid eller karbondioksid når den hydrogenrike gassblandingen fødes som brennstoff til et gasskraftverk. Ved foreliggende oppfinnelse finner reformering av naturgass, skift av karbonmonoksid til karbondioksid og separasjon av gassblandingen til henholdsvis CO₂-rik og H₂-rik gass finne sted ved betingelser som ikke er beskrevet i kjent teknikk. De nevnte betingelsene er likeledes utenfor det som er akseptert og anbefalt i den petrokjemiske industrien.

Ved at fremgangsmåten er kjennetegnet ved et redusert krav til metan og karbonmonoksid i fødestrømmen/råstoffet som føres til bl.a. et gasskraftverk, vil dette medføre at ett eller flere av prosesstrinnene kan foregå ved høyere trykk enn normalt ved reformering av naturgass ved autoterm reformering (ATR), kombinert reformering (CR) eller partiell oksidasjon (POX). Ved at reformer og skift kan foregå ved et høyere trykk oppnås en reduksjon i kapital kostnadene og av kompresjonsenergien av CO₂ før deponering. Det er også mulig å skille ut og komprimere CO₂ i flytende form, noe som kan gi en ytterligere besparelse. Ved foreliggende oppfinnelse kan reformerings- og skift-reaksjonene drives ved lavere temperaturer enn det som ellers ville vært nødvendig/påkrevet ved et gitt trykk. Lavere temperaturer ved et gitt trykk medfører også besparelser. Videre kan det være unødvendig med både lavtemperatur skift og metanisering av rest karbonmonoksid, noe som er standard teknologi i dag ved produksjon av hydrogen for syntese av ammoniakk. En fremgangsmåte for å separere CO₂ kan finne sted ved en aminvaskeprosess, noe som kan fortas i følge foreliggende oppfinnelse ved en forenk-

let fremgangsmåte ved at det benyttes trykkavlastning i stedet for vandampstripping.

Følgende kjemiske reaksjoner finner sted ved fremstilling av syntesegass og hydrogen ved reformering av naturgass:



10

Reaksjonvarmen til den sterkt endoterme dampreformeringsreaksjonen kan tilveiebringes enten ved ekstern fyring, som i en dampreformer, eller ved kombinasjon med den partielle oksidasjonen i en autoterm reformer.

15 I en dampreformer (SR) blir naturgass (metan) konvertert i en rørreaktor ved høy temperatur og relativt lavt trykk. En damp reformer består av et stort antall reaktor rør, 200 – 250 rør med relativ lengde på 12-13 meter, indre diameter på omtrent 10 cm og ytre diameter på omtrent 12 cm. Dette er en plasskrevende enhet med en lengde på 30 – 50 meter, bredde på 10-12 meter og en høyde på 15 – 20 me-
 20 ter. Konvensjonelle dampreformere drives i trykkområdet fra 15 til 30 bar. Utløpstemperaturen på gassen fra en konvensjonell dampreformer ligger i temperaturområdet 950°C. Energien som benyttes til å drive de endoterme reaksjonene tilføres ved ekstern fyring/oppvarming (topp-, side-, bunn- eller terrassefyr). Forholdet mellom damp og karbon er fra 2,5-3,5, og forholdet mellom hydrogen og karbonmonoksid i produktstrømmen er fra 2,7-3,0. En typisk syntesegass produsert fra
 25 en dampreformer inneholdet omkring 3 volum% metan.

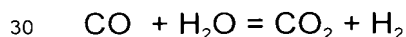
I foreliggende oppfinnelse kan reformeringen av naturgass (ligning 1 og 2 ovenfor) finne sted i en autoterm reformer (ATR). I en ATR fødes naturgass (metan)
 30 sammen med oksygen/luft inn i et forbrenningskammer. Energien som kreves til å drive de endoterme dampreformeringsreaksjonene tilveiebringes ved de eksoterme reaksjonene mellom hydrokarboner/hydrogen og oksygen/luft. Temperaturen i

forbrenningskammeret kan komme opp i over 2000°C. Etter forbrenningskamme-
ret drives reaksjonene til likevekt over en katalysatorsjikt før syntesegassen forla-
ter reaktoren ved rundt 1000°C. Størrelsen på en slik enhet vil kunne være 10-15
meter høy og med en diameter på 5-6 meter. Typisk forhold av damp:karbon er fra
5 0,6-1,4. Forholdet mellom hydrogen karbonmonoksid er lavere enn 2. Typisk me-
tanslipp er 1-2volum% i produktstrømmen. ATR'en kan drives ved høyere trykk
enn SR'en.

Foreliggende oppfinnelse kan også finne sted i en partiell oksidasjonsreaktor
10 (POX) som også er en autoterm reformer foruten at enheten ikke omfatter en ka-
talytatorsjikt. Denne enheten er ofte noe større, dersom samme kapasitet sam-
menlignet med en ATR skal opprettholdes. Årsaken til en noe større reformer er at
ATR'en har katalysator som påskynder de endoterme reaksjonene. Utløpstempe-
raturen for en POX er også noe høyere enn for en typisk ATR.

15 Reformering av naturgass kan også foregå ved kombinert reformering (CR) som
er en kombinasjon av en dampreforming(SR) og en autoterm reformering(ATR).
En kombinasjon av SR og ATR gjør det mulig å justere sammensetning ut av re-
formererenheten ved å regulere pådragene på de to reformerene. SR blir i CR dre-
20 vet ved «mildere» betingelser, dvs. lavere utløpstemperatur, noe som fører til et
høyt metanslipp. Resten av metanet omsettes i ATR'n. Forholdet av damp:karbon
ligger i området 1.8-2.4, med et forhold mellom hydrogen og karbonmonoksid i
produktgassen på over 2.

25 Etter reformering av naturgassen skiftes gassblandingen ifølge foreliggende opp-
finnelse. Gassblandingen fra reformeringsreaktoren inneholder i hovedsak følgen-
de gasskomponenter CO, H₂, H₂O, CO₂ og noe CH₄. Mellom disse fire kompo-
nentene er det en likevektsrelasjon gitt ved den støkiometriske ligningen:



Denne reaksjonen betegnes vannskift-reaksjonen, og ved å drive en skift-reaktor ved bestemte betingelser kan likevekten drives mot høyre og man får en gassblanding som er rik på hydrogen og karbondioksid, og hvor konsentrasjon av karbonmonoksid er lav. Tilstrekkelig hastighet på reaksjonen tilveiebringes ved anvendelse av egnede katalysatorer, og i prosesser der man ønsker høy omsetning av CO (for eks. ammoniakk syntese) benyttes to fixed bed reaktorer i serie, henholdsvis høytemperatur skift reaktor og lav temperatur skift reaktor. To trinn velges fordi likevekten er begunstiget av lav temperatur, mens reaksjonshastigheten er begunstiget av høy temperatur. Ved å velge to reaktorer i serie som arbeider ved ulike temperaturer oppnår man totalt mindre reaktorvolum. Prosessen er tilnærmet trykkuavhengig og det anvendes normalt samme trykk som i reformeren. Typisk temperatur ut av første reaktor er 420 °C og ut av andre reaktor 230°C. Katalysator i første trinn er vanligvis krom/jern-basert, mens katalysatoren i det andre trinnet er vanligvis en kopper/sink katalysator.

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I skiftenheten omsettes CO og H₂O til CO₂ og H₂, og i kjent teknikk er det ofte et krav at nevnte reaksjon i størst mulig grad drives med høyre slik at det er minst mulig CO i gassblandingen ut av skiftenheten. Et lavt CO-innhold i nevnte gassblanding gir igjen en høy renhet av den H₂-rike gasstrømmen ut av separasjonsenheten. I kjent teknikk er vanligvis forholdet mellom H₂O:CO lik 10:1 noe som tilsier et høyt forbruk av H₂O for deretter å oppnå en høy renhet av den H₂-rike gassen. I foreliggende oppfinnelse er det derimot godtagbart med større forurensninger i den H₂-rike gassen noe som medfører et lavere forbruk av H₂O og igjen en enklere skiftprosess. Dette er faktorer som totalt sett gir kostnadsbesparelser ved fremstilling av en CO₂-rik og H₂-rik gasstrøm. I foreliggende oppfinnelse er det godtagbart med et forhold av H₂O:CO på fra 1-9, fortrinnsvis fra 1,5-4.

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Dersom kravet til omsetning av CO₂ er moderat, hvilket vil være tilfelle dersom gassblandingen skal brennes til energiformål, kan man gjennomføre skiftreaksjonen i et trinn. Man kan da velge en enkel høytrykks skift-reaktor.

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Gasser i blanding kan separeres mer eller mindre fullstendig basert på de ulike egenskapene til gassmolekylene. De mest vanlige prinsipper er absorpsjon, adsorpsjon, semipermeable membraner og kryogen destillasjon.

- 5 CO₂ er en sur gass, og den mest brukte fremgangsmåten for å separere nevnte gass fra andre ikke-sure gassmolekyler er absorpsjon. Ved absorpsjon utnyttes de ulike kjemiske egenskapene til gassmolekylene. Ved å bringe gassblandingen i kontakt med en basisk væske vil de sure gassene i stor utstrekning løses i væsken. Væsken skilles fra gassen og den absorberte gassen kan så frigjøres enten
- 10 ved å endre væskens sammensetning eller endre trykk og temperatur. For separasjon av CO₂ er det i hovedsak vandige løsninger av alkoholaminer som benyttes. Absorpsjonen skjer ved relativt lav temperatur og høyt trykk, mens stripping av gassen fra væsken skjer ved relativt høy temperatur og lavt trykk. Ved frigjøring av CO₂ fra amin fasen i strippeenheten anvendes vanligvis strippedamp. Dersom
- 15 partialtrykket av CO₂ i gassen inn på absorpsjonsenheten er høyt f.eks. høyere enn 15 bar er det mulig å oppnå høye konsentrasjoner i aminfasen, og en stor del av absorbert CO₂ kan frigjøres i stripekolonnen ved forhøyet trykk f.eks. 5-8 bar.

Ved bruk av en eller flere semipermeable membranenheter kan man oppnå at

20 molekyler med ulik molvekt og ulike kjemiske egenskaper permeerer membranen med ulik hastighet. Dette prinsippet kan benyttes for å separere gasser. For den aktuelle gassblandingen kan man velge membraner der H₂ permeerer raskt mens CO₂ permeerer langsomt, hvorefter man oppnår en delvis separasjon av de ulike gasskomponentene. Ved å kombinere fast-stoff membraner og væskemembraner

25 er det også mulig å oppnå at CO₂ permeerer raskt mens H₂ holdes tilbake. Ved ulike separasjonsmetoder kan det være vanskelig å oppnå fullstendig separasjon av de ulike gasskomponentene. Dette er spesielt tilfelle ved bruk av membraner. For gassblandinger som skal brennes vil en delvis separasjon av hydrogen og CO₂ være tilstrekkelig.

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I et gasskraftverk forbrennes normalt naturgass der hovedkomponenten er metan og luft i et brennkammer ved forhøyet trykk. Forbrenningsgassene driver turbinene

som skaffer nødvendig akselmoment til kompressordelen (som komprimerer luft til brennkammertrykk) og til drift av generator eller annet mekanisk utstyr. Innblending av naturgass skjer i brennere og design/utforming av disse er viktig for å få riktig flammetemperatur og for å hindre dannelsen av uønskede forbrenningsprodukter. Dersom en hydrogenrik gass benyttes i stedet for naturgass vil man endre flere forhold som er viktig for utforming av brennere, brennkammer og turbin. De viktigste er forbrenningsenergi, flammeforplantningshastighet, eksplosjonsområdet og selvantennelsestemperatur. Dette er forhold som gjør at man ikke uten videre kan benytte en hydrogenrik gass i en gassturbin som er bygget til forbrenning av metan. Erfaringene med forbrenning av hydrogenrike gasser er begrenset, og teknologien er tilgjengelig i begrenset grad.

Ved foreliggende oppfinnelse er det ønskelig å deponere fraseparert CO₂-rik gass. Store mengder CO₂ -rik gass kan deponeres etter flere metoder der de tre mest aktuelle er deponering på store havdyp, deponering i dype vannreservoarer og deponering i oljereservoarer der gassen samtidig fungerer som drivmiddel for økt oljeutvinning. De to siste lagringsformer drives kommersielt. I disse lagringsformer må CO₂ gassen bringes opp til høyt trykk for transport i rørledninger frem til deponeringsbrønn og videre til injisering. Injeksjonstrykket vil variere, men vil kunne ligge i området 50 til 300 bar. Dersom den CO₂ -rike gassen kan separeres fra forhøyet trykk, kan betydelig kompresjonsarbeid spares noe som er tilfelle i foreliggende oppfinnelse.

De vedlagte figurer viser kjent teknikk og ulike utforminger ved foreliggende oppfinnelse.

Figur 1 viser kjent teknikk i form av dampreformering med hydrogenfyring.

Figur 2 viser POX eller ATR med oksygen hvor naturgass (1) forbehandles før denne (2) føres inn på en ATR eller en POX hvor vann (3) og oksyngengass (4) tilsettes. Den reformerte gassblandingen (5) føres deretter videre til en skiftreaktor/skiftenhet hvorefter gassblandingen (6) føres til en separasjonsenhet hvor det fremskaffes en H₂-rik gass (10) og en CO₂-rik gass (7). Strøm (7) kan eventuelt

komprimeres ytterligere før deponering/reinjisering. Strøm (10) kan nyttiggjøres i bl.a. et hydrogenkraftverk.

Figur 3 viser POX eller ATR med luft. Dette er i prinsippet samme prosess som beskrevet i fig.2, men her benyttes luft som oksidant i reformeren i stedet for oksygen. Dette gir noe mildere betingelser enn de man har ved bruk av oksygen i brenner. Ved bruk av luft får man relativt store mengder nitrogen i systemet og partialtrykket av CO_2 vil bli vesentlig lavere. Dette vil igjen gjøre det vanskeligere å ta ut CO_2 ved forhøyet trykk i separasjonsprosessen. Forholdet mellom H_2 og N_2 vil være ca. 1:1.

Eksempel 1:

ATR reaktoren kan drives under ulike driftsbetingelser. I tabellene nedenfor er sammensetningen av gassen ved utløpet av reaktoren vist for ulike trykk, temperaturer og damp/karbon-forhold. I alle beregningene er forholdet oksygen/karbon satt til 0,6. Inngående gass har sammensetning $\text{CO}_2=2,5$; $\text{CH}_4=82$; $\text{C}_2=9$; $\text{C}_3=5$; $\text{C}_{3+}=1,5$.

Tabell 1 viser sammensetning i mol% i tørr gass ved et trykk på 80 bar.

Damp/ karbon	S/C=0,5			S/C=1,8			S/C=2,8		
Temp. °C	800	1000	1200	800	1000	1200	800	1000	1200
H_2	40,9	59	65	52,9	65,6	66,8	58,8	67,9	69,2
CO	13,4	25,9	36,3	10,7	20,8	27,1	9,4	17,7	23,2
CO_2	17,4	7,3	3,8	19	10,9	6,1	19,7	13,1	7,6
C_1	28,2	7,8	1,0	17,5	2,7	0	12,1	1,3	0

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Tabell 2 viser sammensetning i mol% i tørr gass ved et trykk på 120 bar.

Damp/ karbon	S/C=0,5			S/C=1,8			S/C=2,8		
Temp. °C	800	1000	1200	800	1000	1200	800	1000	1200
H ₂	36,6	55,7	64	48,8	63,8	67,0	56	-	69,2
CO	11,7	-	30	9,4	19,9	24,6	7,8	19,4	23
CO ₂	19,4	6,4	4	20,1	11,6	8,0	-	9,6	7,8
C ₁	32,8	11,2	1,9	21,6	4,7	0,4	18,4	0	0

Eksempel 2:

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Eksempel 2 omfatter en ett- trinns skift-reaktor. Gassblandingen inn på skift-reaktoren kan ha varierende sammensetning slik det fremgår av tabellene 1 og 2. Dersom gassammensetningen i tabell 1 ved 1000°C og S/C på 1,8 benyttes vil dette tilsvare et damp/CO forhold ut av ATR-reaktoren på ca. 3,0. Tabell 3 ned-
 15 enfor viser en mulig sammensetning av fødegass og utgående gass fra en ett-trinns skift-reaktor som har en utløpstemperatur på 400°C.

Tabell 3 viser gassammensetning fra en ett-trinns skift-reaktor gitt i mol pr. 100 mol tørr gass.

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Komponent	Fødegass	Utgående gass
H ₂	65,6	70,8
CO	20,8	2,4
CO ₂	10,9	24,5

C1	2,7	2,3
H ₂ O	62,4	37,3

Eksempel 3:

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Eksempelen omfatter en to- trinns skift-reaktor. Dersom to-trinns skift-reaktor benyttes vil man oppnå høyere omsetning av CO. Tabell 4 viser en mulig gassammensetning for en to-trinns prosess der utløpstemperaturen i første reaktor er 400° C og i andre reaktor er 250 C. Inngående gass har samme sammensetning som i eksempel 2.

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Tabell 4: Mulig gassammensetning for en to-trinns prosess gitt i mol pr. 100 mol tørr gass.

Komponent	Fødegass	Utgående gass
H ₂	65,6	71,5
CO	20,8	0,3
CO ₂	10,9	26,0
C ₁	2,7	2,2
H ₂ O	62,4	35

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Eksempel 4:

Separasjon av CO₂ ved absorpsjon i etanolaminløsning (aminvask) er beskrevet i dette eksempelet. Gassblandingen ut fra skift reaktoren inneholder betydelige mengder vanndamp. Etter avkjøling til f.eks. 40°C vil det meste av vanndampen kondenseres ut, og nedenfor er to typer mulige gassblandinger fra reformeringsprosessen vist:

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Tabell 5. Mulige gassammensetninger fra reformerprosessen .

Komponent	Gass 1	Gass 2
CH ₄	3 mol%	3 mol%
CO	2 mol%	2 mol%
CO ₂	17,7 mol%	29 mol%
H ₂	62,3 mol%	66 mol%
Totaltrykk	40 bar	80 bar

Disse gassblandingerne kan fødes til en absorpsjonskolonne der en vandig meta-
 10 nolaminløsning brukes som absorpsjonsvæske. Aminløsningen vil absorbere ho-
 veddelen av CO₂ og gassen ut fra absorpsjonskolonnen vil bestå hovedsakelig av
 hydrogen. Den CO₂ rike aminløsningen fødes til en strippe-enhet der trykket er
 f.eks. 8 bar og temperaturen er f.eks. 120°C. En andel av CO₂-gassen vil frigjøres
 på grunn av temperaturøkningen og trykkreduksjonen. Ytterligere CO₂ kan frigjø-
 15 res fra aminløsningen ved stripping med vanndamp.

Tabell 6 nedenfor viser en mulig sammensetning av gassfase ut fra absorp-
 sjonskolonnen og ut fra strippe enheten når gass av type 2 i tabell 5 benyttes som
 føde og det kun benyttes trykkreduksjon og temperaturøkning og ingen strippe-
 20 damp.

Tabell 6 viser sammensetning av gass fra absorpsjonsenhet og strippenhet uten
 bruk av strippedamp.

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Komponent	Ut fra abs. kolonne	Ut fra strippekolonne
CH ₄	4 mol%	-
CO	3 mol%	-
H ₂ O	-	30 mol%
CO ₂	3 mol%	70 mol%
H ₂	90 mol%	-
Totaltrykk	80 bar	8 bar
Temperatur	50°C	120°C

Eksempel 5:

Eksempel 5 vedrører separasjon ved kondensasjon. Ved nedkjøling av en CO₂ rik gass vil CO₂ kunne kondenseres ut som væske eller felles ut som fast stoff (CO₂ is) . Ved en temperatur på -57 °C nåes frysepunktet for CO₂ og damptrykket av CO₂ er da 5,1 bar. Kjøles CO₂ gass ytterligere fåes fast CO₂ og ved -78° C er damptrykket over fast CO₂ 1 bar.

Gass av type 2 i tabell 5 tørkes helt fri for vann før den behandles i en kondensatorenhet bestående av flere kjøletrinn, der temperaturen på gassen i første kjøletrinn reduseres til ca. -55° C. Ved denne temperaturen vil en stor del av CO₂ kondensere ut og gassammensetningen ut fra kondensatoren kan være som vist i kolonne 2 i tabellen nedenfor:

Tabell 7 viser sammensetning av gassfaser i to-trinns kjøleprosess.

Komponent Sammensetning av gass	Sammensetning av gass	
	Fra kjøletrinn 1	Fra kjøletrinn 2
CH ₄	3,5 mol%	3,8 mol%
CO	2,3 mol%	2,5 mol%
N ₂	0,2 mol%	0,2 mol%
CO ₂	7,5 mol%	1,0 mol%
H ₂	86,7 mol%	92,5 mol%
Totaltrykk	80 bar	80 bar

I dette talleksempellet vil ca. 70% av CO₂ i inngående gass bli kondensert ut i kjøletrinn 1. Ved ytterligere senking av temperaturen i en ny prosessenhet (kjøletrinn 2) til f.eks. - 80° C vil gassammensetningen ut kunne bli som vist i kolonne tre i tabell 7 ovenfor. Ved hjelp av de to kjøletrinnene kan 96% av CO₂ i inngående gass fjernes. Den utkondenserte væske og det utfelte faste stoff vil være tilnærmet rent CO₂.

Eksempel 6:

Dette eksempelet beskriver kompresjon av CO₂. Gassfasen fra strippe-enheten i eksempel 4 inneholder vanndamp og CO₂. Ved kjøling av denne gassen til f.eks. 40 °C vil det meste av vanndampen kondenseres ut og den tilnærmet rene gassen ved et trykk på 8 bar kan komprimeres til ønsket leveringstrykk for transport av CO₂ i rørledning.

Eksempel 7:

Eksempellet vedrører ved en eller flere membranenheter hvor den CO₂-rike gassen kan ha et trykk omtrent lik partialtrykket av CO₂ inn på separasjonsenheten noe som er vist i tabell 1 nedenfor.

Det totale innløpstrykket på separasjonsenheten (bar)	Partialtrykket av CO2 ut fra separasjonsenheten (bar)
200	40
250	50
300	60

Patentkrav

1. Fremgangsmåte for fremstilling av en CO_2 -rik gasstrøm og en H_2 -rik gasstrøm, karakterisert ved at fremgangsmåten omfatter følgende trinn:

- 5 a) naturgass og vann fødes til en reformeringsreaktor og omdannes til syntesegass under tilførsel av en O_2 -holdig gass;
- b) gasstrømmen fra a) skiftes, hvor innholdet av CO reduseres og mengden av CO_2 og H_2 økes ved omsetning av H_2O ;
- c) gasstrømmen fra b) separeres i en separasjonsenhet i henholdsvis en
10 CO_2 -rik og en H_2 -rik gasstrøm.

2. Fremgangsmåte ifølge krav 1, karakterisert ved at skiftprosessen i b) utføres i ett trinn.

15 3. Fremgangsmåte ifølge kravene 1-2, karakterisert ved at forholdet av $\text{H}_2\text{O}:\text{CO}$ i skiftprosessen er fra 1 til 9.

4. Fremgangsmåte ifølge kravene 1-3, karakterisert ved at forholdet av $\text{H}_2\text{O}:\text{CO}$ i skiftprosessen fortrinnsvis er fra 1,5 til 4.

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5. Fremgangsmåte ifølge kravene 1-4, karakterisert ved at trykket i den CO_2 -rike gasstrømmen etter separasjonsenheten er fra 1 til 100 bar.

6. Fremgangsmåte ifølge kravene 1-5, karakterisert ved at trykket i
25 den CO_2 -rike gasstrømmen etter separasjonsenheten er fra 5 til 50 bar.

7. Fremgangsmåte ifølge kravene 1-6, karakterisert ved at karbonandel i den H_2 -rike gasstrøm er fra 1 til 20 volum%.

30 8. Fremgangsmåte ifølge kravene 1-7, karakterisert ved at karbonandel i den H_2 -rike gasstrøm er fra 5 til 15 volum%.

9. Fremgangsmåte ifølge kravene 1-8, k a r a k t e r i s e r t v e d a t ved at naturgassen i trinn a) tilføres en oksygenrik gass.

5 10. Fremgangsmåte ifølge kravene 1-8, k a r a k t e r i s e r t v e d a t ved at naturgassen i trinn a) tilføres luft/oksygenanriket luft.

11. Fremgangsmåte ifølge kravene 1-8, k a r a k t e r i s e r t v e d a t reformeringsreaktoren fortrinnsvis er en partiell oksidasjonsreaktor.

10 12. Fremgangsmåte ifølge kravene 1-11, k a r a k t e r i s e r t v e d a t reformeringsreaktoren særlig er en autoterm reformer.

15 13. Fremgangsmåte ifølge krav 12, k a r a k t e r i s e r t v e d a t gasstrømmen fra et forbrenningskammer i en autoterm reformer bringes i kontakt med et katalysatorsjikt.

14. Fremgangsmåte ifølge krav 11, k a r a k t e r i s e r t v e d a t reformeringen utføres uten katalysator.

20 15. Fremgangsmåte ifølge kravene 1-14, k a r a k t e r i s e r t v e d a t gassstrømmen ut fra reformeren har en temperatur i intervallet fra 800 til 1200°C.

25 16. Fremgangsmåte ifølge krav 10, k a r a k t e r i s e r t v e d a t minst en andel N₂ følger den CO₂-rike gasstrømmen.

17. Anvendelse av CO₂-rik gasstrøm fremstilt ifølge krav 1 for injeksjon i marine formasjoner.

18. Anvendelse av H₂-rik gasstrøm fremstilt ifølge krav 1 for hydrogenering.

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19. Anvendelse av H₂ -rik gasstrøm fremstilt ifølge krav 1 som energikilde/drivstoff i brenselceller.

20. Anvendelse av H_2 -rik gasstrøm fremstilt ifølge krav 1 for elektrisitetsproduksjon

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S a m m e n d r a g

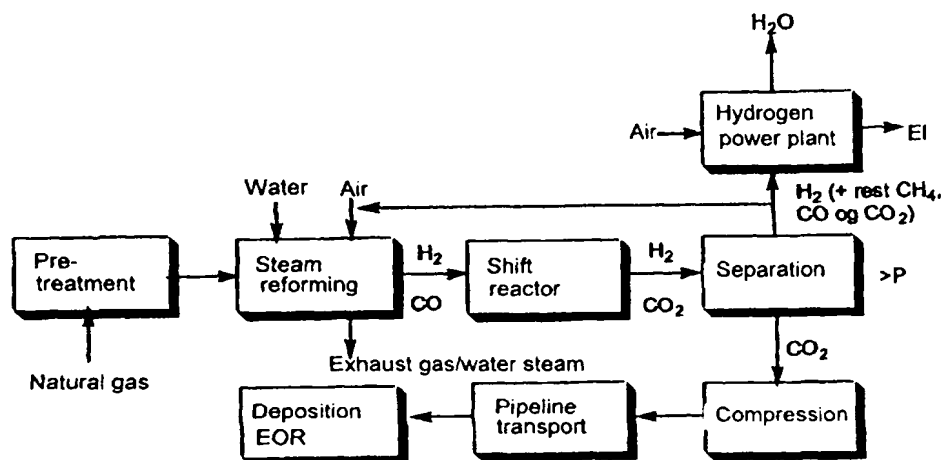
Foreliggende oppfinnelse omfatter en fremgangsmåte for fremstilling av en CO_2 -rik gasstrøm og en H_2 -rik gasstrøm, hvor fremgangsmåten omfatter følgende trinn:

- a) naturgass og vann fødes til en reformeringsreaktor og omdannes til syntesegass under tilførsel av en O_2 -holdig gass;
- b) gasstrømmen fra a) skiftes, hvor innholdet av CO reduseres og mengden av CO_2 og H_2 økes ved omsetning av H_2O ;
- c) gasstrømmen fra b) separeres i en separasjonsenhet i henholdsvis en CO_2 -rik og en H_2 -rik gasstrøm.

Oppfinnelsen vedrører også anvendelse av CO_2 -rik gasstrøm for injeksjon i marine formasjoner samt anvendelse av H_2 -rik gasstrøm for hydrogenering, som energikilde/drivstoff i brenselceller eller for elektrisitetsproduksjon.

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(54) Title: PROCESS FOR PREPARING A H₂-RICH GAS AND A CO₂-RICH GAS AT HIGH PRESSURE

shows known technique in the form of steam reforming with hydrogen firing

(57) Abstract

The present invention comprises a method for production of a CO₂-rich gas stream and a H₂-rich gas stream, the method comprising the following steps: a) natural gas and water are fed to a reforming reactor and are converted to synthesis gas under supply of a O₂-containing gas; b) the gas stream from a) is shifted, whereby the content of CO is reduced and the amounts of CO₂ and H₂ are increased by reaction of H₂O; c) the gas stream from b) is separated in a separation unit into a CO₂-rich and a H₂-rich gas stream, respectively. The invention also concerns the use of a CO₂-rich gas stream for injection into marine formations, and the use of a H₂-rich gas stream for hydrogenation, as a source of energy/fuel in fuel cells or for production of electricity.

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Method for preparing a H₂-rich gas and a CO₂-rich gas at high pressure.

The present invention comprises a method for production of a CO₂-rich gas for injection purposes or to be deposited, and a hydrogen-rich gas, as well as use thereof.

It is commonly assumed that the greenhouse effect and the climate on earth are closely connected to human made emissions of CO₂. These emissions are primarily
5 formed by combustion of coal and hydrocarbons, i.a. by generation of heat and electric power. A desirable goal is therefore to reduce the emission of CO₂ to the atmosphere.

It is known art to reduce the emission of CO₂ from combustion of natural gas, e.g. by gas reforming and shift technology for preparation of a mixture consisting of hydrogen
10 and carbon dioxide. These components are then separated, whereafter hydrogen is used as fuel in a gas turbine and carbon dioxide is deposited after compression to desired pressure. The deposition can be made on the bottom of the sea or in geological reservoirs. The reservoirs can also contain hydrocarbons. The above mentioned technique is i.a. described in Teknisk Ukeblad No. 16, page 8, 1998.

15 Known art comprising gas reforming and shift technology as described above is very expensive while providing less energy yield than a conventional, modern gas power plant.

US 3,652,454 describes preparation of CO₂ and H₂ from a gas stream containing CO by an improved continuous catalytical shift reaction at high pressure. The reaction
20 takes place in one or more shift reactors at a superatmospheric pressure of from 35 to 250 atmospheres, and a temperature between 287°C and 537°C. The patent does not describe reforming of natural gas.

From EP 0 000 993-A1 it is known a method for preparation of ammonia by means of a primary and a secondary catalytic reforming of an hydrocarbon stream at superatmospheric pressure. From the primary catalytic reforming the ratio of steam to carbon
25 is from 2.5 to 3.5, the pressure is from 30 to 120 bar and the temperature out of the reactor is from 750 to 850°C. From the secondary catalytic reforming the content of methane is from 0.2 to 10 % by weight on a dry basis and the ratio of hydrogen to nitrogen is from 2.2 to 2.7. To the secondary reforming there is added an excess of air for
30 preparing a gas with a higher content of methane, i.e. at a lower temperature, and/or a lower steam ratio and/or a higher pressure. In the above mentioned EP patent CO₂ is re-

moved at a low pressure by taking out hydrogen at an elevated pressure for further use by the preparation of ammonia.

EP 0 289 419 describes catalytic steam reforming of hydrocarbons for preparing hydrogen in an ammonia process. The catalytic steam reforming takes place at a pressure from 25 to 120 bar, a temperature from 800 to 1000°C and at a ratio steam:carbon of 1.8-2.5. The process is operated in such a way that there are less than 0.3% impurities in the H₂-rich gas which is to be used for production of ammonia. The present invention allows a higher content than 0.3% of CO, CO₂ and CH₄ in the H₂-rich gas stream.

CA 868,821 describes the preparation of synthesis gas by steam reforming of hydrocarbons in a gas and a liquid at 50-250 absolute atmospheres, preferably 160 abs. atm. for production of ammonia and methanol.

Known art does not deal with a simplified plant as comprised by the present invention, where natural gas is reformed at high pressure in an autothermal reformer followed by a shift reactor, whereafter a CO₂-rich gas is provided at a pressure in the interval from 1 to 100 bar, which leads to reduced compression costs by deposition and reinjection. The simplified plant results in that a limited part of the carbon in the raw material is in the form of methane or carbon monoxide when the hydrogen-rich gas mixture is fed as a fuel to a gas power plant. A result of the reduced demand to the purity of the product gas involves that one or more of the process steps can be operated at a higher pressure, a lower temperature and/or a lower ratio steam/carbon.

The present invention comprises a method for production of a CO₂-rich gas stream and a H₂-rich gas stream, whereby the method is characterized by the following steps:

- a) natural gas and water are fed to a reforming reactor and are converted to synthesis gas under supply of a O₂-containing gas;
- b) the gas stream from a) is shifted, whereby the content of CO is reduced and the amounts of CO₂ and H₂ are increased by reaction of H₂O;
- c) the gas stream from b) is separated in a separation unit into a CO₂-rich and a H₂-rich gas-stream, respectively.

It is a further object of the present invention that the shift process in b) is carried out in one step where the ratio H₂O:CO in the shift process can be from 1 to 9, preferably 1.5 to 4. In the present invention the pressure in the CO₂-rich gas stream after the separation unit is from 1 to 100 bar, preferably from 5 to 50 bar. The carbon part in the H₂-rich

gas stream is from 1 to 20 % by volume, preferably from 5 to 15 % by volume. The invention is characterized in that to the natural gas in step a) it is added an oxygen rich gas or air/oxygen enriched air stream. The reforming reactor according to the invention is preferably a partial oxidation reactor, especially an autothermal reformer. The gas stream from a combustion chamber in an autothermal reformer is brought in contact with a catalyst bed. When the reforming takes place in an partial oxidation reactor, the reaction is carried out without a catalyst. Further, the gas stream out of the reformer has a temperature within the interval from 800 to 1200°C. When the natural gas in step a) is supplied with air/oxygen enriched air at least a part of N₂ follows the CO₂-rich gas stream through the process. The present invention also concerns the use of the CO₂-rich gas stream prepared according to the previously mentioned method, where the CO₂-rich gas stream is injected into marine formations. Further, the invention comprises the use of the H₂-rich gas stream prepared according to the invention, where the H₂-rich gas stream can be utilized for hydrogenation, in the production of electricity and as a source of energy / fuel in fuel cells.

An important feature of the invention is that the CO₂-rich stream is present at an elevated pressure, which means that the compression work which is necessary to bring the pressure up to the injection pressure or deposition pressure (50-250 bar) becomes as little as possible. This requires a high pressure through all units (reformer, shift unit and separator unit). As an example the natural gas which is fed into the reformer can have a pressure of 30-200 bar. By a marginal pressure drop in the reformer and the shift unit, the pressure into the separation unit will be within the same interval.

The present invention provides several advantages when producing a H₂-rich and a CO₂-rich gas, respectively. One of the advantages is that increased pressure gives increased reaction for each volume unit in reformer and shift reactor, and further a reduced compression work of CO₂ by a possible reinjection or deposition. In addition, increased pressure gives reduced compression work for feed to the gas turbine. In the reformer there is high primary formation of CO₂ as a result of high pressure. Another advantage of the present invention is a simplified design and operation of a possible a gas turbine for combustion of the H₂-rich gas stream as a result of a certain slip of CH₄ in the reformer, CO in the shift reactor and CO₂ in the separation step. The use of air or oxygen enriched air in the case of an autothermal reformer (ATR) and partial oxidation (POX) give savings in oxygen units and gives a simplified design and operation of ATR and gas turbine. A cer-

tain CO slip, i.e. not reacted gas component, makes low temperature shift and methanation unnecessary. In the present invention it might be necessary to supply steam to the shift reactor. A certain slip of CO₂ in the present invention simplifies the separation process. If the separation is carried out with amine washing, a moderate pressure release might be sufficient.

The present invention comprises a number of embodiments where i.a. natural gas is cleaned and pre-treated in a suitable manner so that the gas feed mainly will consist of methane after treatment. The reforming takes place at a pressure within the interval 30 to 200 bar. It is preferred to use a shift reactor when carrying out the present invention.

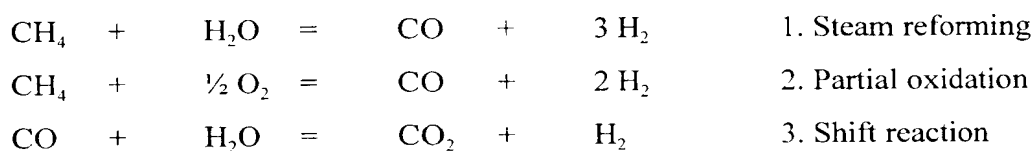
Steam can be supplied to the shift reactor, but it can also be operated without supply of steam. At the outlet of the shift reactor a content on carbon basis of CO up to 2 % by volume, preferably 5 % by volume, and methane with 2 % by volume, preferably 5 % by volume, is acceptable. Further, the H₂-rich gas stream according to the invention can contain at least 1 % by volume and up to maximum 20 % by volume of the original amount of carbon in the natural gas. The steam reformer can be fired with the hydrogen rich fuel gas. If autothermal reforming is used at least a part of the hydrogen rich stream can be used for pre-heating of the feed gas. Pre-heating of the feed gas can also be carried out by heat exchange with warm gas from a gas turbine.

The object of the present invention is that a limited part of the carbon in the feed stream/raw material is in the form of methane, carbon monoxide or carbon dioxide when the hydrogen rich gas mixture is fed as fuel to a gas power plant. In the present invention reforming of natural gas, shift of carbon monoxide to carbon dioxide and separation of the gas mixture into CO₂-rich and H₂-rich gas, respectively, takes place at conditions which have not been described in known technique. The mentioned conditions are also outside of those which is accepted and recommended in the petrochemical industry.

Because the method is characterized by a reduced requirement to methane and carbon monoxide in the feed stream/raw material which i.a. is passed to a gas power plant, this will involve that one or more of the process steps can take place at higher pressure than normal for reforming of natural gas by autothermal reforming (ATR), combined reforming (CR) or partial oxidation (POX). The fact that reforming and shift can take place at a higher pressure leads to a reduction in capital costs and in compression energy for CO₂ before deposition. It is also possible to separate out and compress CO₂ in liquid form,

which can give further savings. In the present invention the reforming and shift reactions can be carried out at lower temperatures than those being necessary/required at a given pressure. Lower temperatures at a given pressure also lead to savings. Further it can be unnecessary with both low temperature shift and methanation of residual carbon monoxide, which is standard technology today in production of hydrogen for synthesis of ammonia. A method to separate CO_2 can be by an amine washing process, which in the present invention can be carried out by a simplified method by using pressure release instead of steam stripping.

The following chemical reactions take place by production of synthesis gas and hydrogen by reforming of natural gas:



The heat of reaction for the strongly endothermic steam reforming can be provided either by external heating, as in a steam reformer, or by combination with the partial oxidation in an autothermal reformer.

In steam reformer (SR) natural gas (methane) is converted in a tube reactor at high temperature and relatively low pressure. A steam reformer consists of many reactor tubes, i.e. 200 – 250 tubes with relative lengths of 12-13 metres, inside diameter of about 10 cm and an outside diameter of about 12 cm. This is a space demanding unit with a length of 30 – 50 metres, width of 10-12 metres and a height of 15 – 20 metres. Conventional steam reformers are operated in the pressure range from 15 to 30 bar. The outlet temperature of the gas from a conventional steam reformer lies in the temperature area 950°C . The energy which is used to carry out the endothermic reactions is supplied by external firing/heating (top-, side-, bottom- or terrace-fired). The ratio between steam and carbon is from 2.5 to 3.5, and the ratio between hydrogen and carbon monoxide in the product stream is from 2.7 to 3.0. A typical synthesis gas produced from a steam reformer contains approximately 3 % by volume of methane.

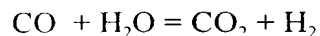
In the present invention the reforming of natural gas (equation 1 and 2 above) can take place in an autothermal reformer (ATR). In an ATR natural gas (methane) is fed together with oxygen/air into a combustion chamber. The energy which is required to operate the endothermic steam reforming reactions is provided by the exothermic reacti-

ons between hydrocarbons/hydrogen and oxygen/air. The temperature i the combustion chamber can reach more than 2000°C. After the combustion chamber the reactions are driven to equilibrium over a catalyst bed before the synthesis gas is leavig the reactor at approximately 1000°C. The size of such a unit could be a height of 10-15 metres and a diameter of 5-6 metres. Typical ratio of steam:carbon is from 0.6 to 1.4. The ratio between hydrogen and carbon monoxide is lower than 2. Typical methane slip is 1-2% by volume i the product stream. The ATR can be operated at higher pressure than the SR.

The present invention can also take place in a partial oxidation reactor (POX) which also is an autothermal reformer except that the unit does not comprise a catalyst bed. This unit is often somewhat bigger if the same capacity compared to an ATR shall be maintained. The reason for a somewhat bigger reformer is that the ATR has catalyst which make the endothermic reactions more rapid. The exit temperature for a POX is also somewhat higher than for a typical ATR.

Reforming of natural gas can also be made by combined reforming (CR) which is a combination of a steam reforming (SR) and an autothermal reforming (ATR). A combination of SR and ATR makes it possible to adjust the composition out of the reformer unit by regulating the efforts on the two reformers. SR is in CR operated at «milder» conditions, i.e. lower outlet temperature, which leads to a high methane slip. The residual methane is reacted in the ATR. The ratio steam:carbon is in the area 1.8-2.4, with a ratio between hydrogen and carbon monoxide in the product gas higher than 2.

After reforming of the natural gas the gas mixture according to the present invention is shifted. The gas mixture from the reformer reactor contains mainly the gas components CO, H₂, H₂O, CO₂ and some CH₄. Between these components there is an equilibrium relation given by the stoichiometric equation:



This reaction is called the water shift reaction, and by operating a shift reactor at certain conditions the equilibrium can be forced to the right and a gas mixture is obtained which is rich in hydrogen and carbon dioxide, and where the concentration of carbon monoxide is low. Sufficient reaction velocity is provided by use of suitable catalysts, and in processes where a high degree of reaction of CO is desirable (e.g. ammonia synthesis) two fixed bed reactors are used in series, high temperature shift reactor and low temperature shift reactor, respectively. Two steps are chosen because the equilibrium is favoured by low

temperature, whereas the reaction velocity is favoured by high temperature. By selecting two reactors working in series, a smaller total reactor volume is achieved. The process is nearly pressure independent and normally the same pressure as in the reformer is used. Typical temperature out of the first reactor is 420°C and out of the second reactor 230°C. Catalyst in the first step is normally based on chromium/iron, whereas the catalyst in the second step normally is a copper/zinc catalyst.

In the shift unit CO and H₂O are reacted to CO₂ and H₂, and in known technique it is often a requirement that the mentioned reaction to a highest possible degree is driven to the right, so that as little CO as possible is present in the gas mixture out of the shift unit. A low content of CO in the mentioned gas mixture again gives a high purity of the H₂-rich gas stream out of the separation unit. In known art the ratio H₂O:CO is usually equal to 10:1, which gives a high consumption of H₂O, for thereafter to obtain a high purity of the H₂-rich gas. In the present invention it is, however, acceptable with more impurities in the H₂-rich gas, which implies a lower consumption of H₂O and again a simpler shift process. These are factors which gives total cost savings by the production of a CO₂-rich and H₂-rich gas stream. In the present invention it is acceptable with a ratio H₂O:CO of from 1 to 9, preferably from 1.5 to 4.

If the requirement to reaction of CO₂ is moderate, which will be the case if the gas mixture shall be burned for energy purposes, the shift reaction can be carried out in one step. A simple high pressure shift reactor can then be selected.

Gases in mixture can be separated more or less completely based on the different properties of the gas molecules. The most common principles are absorption, adsorption, semipermeable membranes and kryogenic distillation.

CO₂ is an acid gas, and the most widely used method to separate the mentioned gas from other non-acid gas molecules is absorption. During absorption the different chemical properties of the gas molecules are utilized. By contacting the gas mixture with a basic liquid the acid gases will to a high degree be dissolved in the liquid. The liquid is separated from the gas and the absorbed gas can then be set free either by altering the composition of the liquid or by altering pressure and temperature. For separation of CO₂ mainly aqueous solutions of alcoholamines are used. The absorption is taking place at a relatively low temperature and a high pressure, while stripping of the gas from the liquid is carried out at a relatively high temperature and low pressure. To liberate CO₂ from the

amine phase in the stripping unit, stripping steam is usually used. If the partial pressure of CO_2 in the gas into the absorber is high, e.g. higher than 15 bar, it is possible to obtain high concentrations in the amine phase, and a large part of absorbed CO_2 can be set free in the stripping unit at elevated pressure, e.g. 5-8 bar.

5 By the use of one or more semipermeable membrane units it is possible to achieve that molecules of different molecular weight and different properties permeate the membrane at different velocities. This principle can be utilized to separate gases. For the gas mixture in question membranes can be selected where H_2 permeates rapidly, whereas CO_2 permeates slowly, whereafter a separation-in-part of the different gas components is
10 achieved. By combining solid membranes and liquid membranes it is also possible to achieve a rapid permeation of CO_2 , while H_2 is kept back. It can be difficult to achieve complete separation of the different gas components by using different separation methods. This is especially the case by the use of membranes. For gas mixtures which are to be burned, a partly separation of hydrogen and CO_2 will be sufficient.

15 In a gas power plant normally natural gas is burned wherein the main component is methane, and air in a combustion chamber at elevated pressure. The combustion gases are driving the turbines which provide necessary shaft moment to the compressor part (which compresses air to the pressure of the combustion chamber) and to operate the generator or other mechanical equipment. Mixing in of natural gas takes place in burners
20 and design/construction of these is important in order to obtain correct flame temperature and to prevent formation of undesired combustion products. If a hydrogen rich gas is used instead of a natural gas, more conditions which are necessary for the construction of burners, combustion chamber and turbine, will be changed. The most important are combustion energy, flame propagation velocity, explosion range and auto ignition temperature.
25 re. These are conditions which lead to the fact that a hydrogen rich gas cannot be used in a gas turbine which is constructed for combustion of methane without modifications. The experience in burning hydrogen rich gases is limited, and the technology is available to a delimited extent.

In the present invention it is desirable to deposit out-separated CO_2 . Large
30 amounts of CO_2 can be deposited according to various methods, of which the three most interesting are deposition at very deep oceans, deposition in deep water reservoirs and deposition in oil reservoirs wherein the gas at the same time functions as drive agent for

enhanced oil recovery. The two last mentioned storage methods are operated commercially. In these storage forms the CO_2 gas has to be brought to high pressure for transport in pipelines to a deposition well and further to injection. The injection pressure will vary, but could be in the range 50 to 300 bar. If the CO_2 gas can be separated from the H_2/CO_2 mixture at an elevated pressure, significant compression work can be avoided, and this is the case in the present invention.

The attached figures show known technique and different embodiments of the present invention.

Figur 1 shows known technique in the form of steam reforming with hydrogen firing.

Figur 2 shows POX or ATR with oxygen where natural gas (1) is pre-treated before this (2) and is passed into an ATR or a POX where water (3) and oxygen gas (4) are added. The reformed gas mixture (5) is thereafter passed to a shift reactor/shift unit whereafter the gas mixture (6) is passed to a separation unit where a H_2 -rich gas (10) and a CO_2 -rich gas (7) are provided. Stream (7) can possibly be compressed further before deposition/reinjection. Stream (10) can be utilized i.a. a hydrogen power plant.

Figure 3 shows POX or ATR with air. This is in principle the same process as described in Figure 2, but in this case air is used as oxidant in the reformer instead of oxygen. This gives somewhat milder conditions than those present by the use of oxygen in the burner. By the use of air relatively big amounts of nitrogen gets into the system and the partial pressure of CO_2 will be considerably lower. This again will render it more difficult to take out CO_2 at an elevated pressure in the separation process. The ratio between H_2 and N_2 will be approximately 1:1.

Example 1

The ATR reactor can be operated under different operating conditions. In the tables below the composition of the gas at the outlet of the reactor is shown for different pressures, temperatures and steam/carbon ratios. In all calculations the ratio oxygen/carbon is set at 0.6. Feed gas has the composition $\text{CO}_2=2.5$; $\text{CH}_4=82$; $\text{C}_2=9$; $\text{C}_3=5$; $\text{C}_{3+}=1.5$.

Table 1 shows composition in mole% in dry gas at a pressure of 80 bar

Steam/carbon	S/C=0.5			S/C=1.8			S/C=2.8		
Temp. °C	800	1000	1200	800	1000	1200	800	1000	1200
H ₂	40.9	59	65	52.9	65.6	66.8	58.8	67.9	69.2
CO	13.4	25.9	36.3	10.7	20.8	27.1	9.4	17.7	23.2
CO ₂	17.4	7.3	3.8	19	10.9	6.1	19.7	13.1	7.6
C ₁	28.2	7.8	1.0	17.5	2.7	0	12.1	1.3	0

Table 2 shows composition in mole% in dry gas at a pressure of 120 bar

Steam/carbon	S/C=0.5			S/C=1.8			S/C=2.8		
Temp. °C	800	1000	1200	800	1000	1200	800	1000	1200
H ₂	36.6	55.7	64	48.8	63.8	67.0	56	-	69.2
CO	11.7	-	30	9.4	19.9	24.6	7.8	19.4	23
CO ₂	19.4	6.4	4	20.1	11.6	8.0	-	9.6	7.8
C ₁	32.8	11.2	1.9	21.6	4.7	0.4	18.4	0	0

5

Example 2

Example 2 comprises a one step shift reactor. The gas mixture into the shift reactor can have a varying composition as is evident from the Tables 1 and 2. If the gas composition in Table 1 is used at 1000°C and S/C of 1.8, this will correspond to a steam/CO ratio out of the ATR reactor of about 3.0. Table 3 below shows a possible composition of feed gas and outcoming gas from a one step shift reactor having an outlet temperature of 400°C.

10

Table 3 shows the gas composition from an one step shift reactor given in moles/100 moles dry gas.

Component	Feed gas	Leaving gas
H ₂	65.6	70.8
CO	20.8	2.4
CO ₂	10.9	24.5
C ₁	2.7	2.3
H ₂ O	62.4	37.3

Example 3

5 The example comprises a two step shift reactor. If a two step shift reactor is used, higher degree reaction of CO will be obtained. Table 4 shows a possible gas composition for a two step process where the outlet temperature in the first reactor is 400° C and in the second reactor 250°C. Inflowing gas has the same composition as in example 2.

Table 4: Possible gas composition for a two step process given in moles/100 moles dry gas.

Component	Feed gas	Leaving gas
H ₂	65.6	71.5
CO	20.8	0.3
CO ₂	10.9	26.0
C ₁	2.7	2.2
H ₂ O	62.4	35

Example 4

10 Separation of CO₂ by absorption i etanolamine solution (amine washing) is described in this example. The gas mixture out from the shift reactor contains significant

amounts of steam. After cooling to e.g. 40°C most of the steam will be condensed out, and below two types of possible gas mixtures from the reforming process are shown:

Table 5: Possible gas compositions from the reforming process

Component	Gas 1	Gas 2
CH ₄	3 mol%	3 mol%
CO	2 mol%	2 mol%
CO ₂	17.7 mol%	29 mol%
H ₂	62.3 mol%	66 mol%
Total pressure	40 bar	80 bar

5 These gas mixtures can be fed to an absorption column where an aqueous methanolamine solution is used as absorption liquid. The amine solution will absorb the main part of CO₂, and the gas out of the absorption column will mainly consist of hydrogen. The CO₂ rich amine solution is fed to a stripping unit where the pressure is e.g. 8 bar and the temperature is e.g. 120°C. A part of the CO₂ gas will be liberated because of the temperature increase and the pressure reduction. Further CO₂ can be set free from the amine solution by stripping with steam.

10 Table 6 below shows a possible composition of the gas phase out from the absorption column and out from the stripping unit when gas of type 2 in Table 5 is used as feed and only pressure reduction and temperature increase is used and no stripping steam.

Table 6 shows the composition of gas from absorber unit and stripping unit without use of stripping steam.

Component	Out from absorption column	Out from stripping column
CH ₄	4 mol%	-
CO	3 mol%	-
H ₂ O	-	30 mol%
CO ₂	3 mol%	70 mol%
H ₂	90 mol%	-
Total pressure	80 bar	8 bar
Temperature	50°C	120°C

Example 5

Example 5 concerns separation by condensation. By cooling of a CO₂-rich gas CO₂ could be condensed out as a liquid or precipitated as a solid (CO₂ ice). At a temperature of -57°C the freezing point of CO₂ is reached and the vapour pressure of CO₂ is then 5.1 bar. If CO₂ gas is further cooled, solid CO₂ is obtained and at -78°C the vapour pressure over solid CO₂ is 1 bar.

Gas of type 2 in Table 5 is dried completely free of water before it is treated in a condenser unit consisting of more cooling steps, wherein the temperature of the gas in the first cooling step is reduced to about -55° C. At this temperature a big part of the CO₂ will condense out and the gas composition out from the condenser can be as shown in column 2 in the table below:

Table 7 shows the composition of gas phases in a two step cooling process

Component Composition of gas	Composition of gas	
	From cooling step 1	From cooling step 2
CH ₄	3.5 mol%	3.8 mol%
CO	2.3 mol%	2.5 mol%
N ₂	0.2 mol%	0.2 mol%
CO ₂	7.5 mol%	1.0 mol%
H ₂	86.7 mol%	92.5 mol%
Total pressure	80 bar	80 bar

In this example about 70% av CO₂ in the incoming gas will be condensed out in cooling step 1. By lowering the temperature further in a new process unit (cooling step 2) to e.g. -80°C the gas composition could be as shown in column 3 in Table 7 above. By means of the two cooling steps 96% of CO₂ in the incoming gas can be removed. The out-condensed liquid and the precipitated solid will be nearly pure CO₂.

Example 6

This example describes compression of CO₂. The gas phase from the stripping unit in example 4 contains steam and CO₂. By cooling of this gas to e.g. 40°C, most of the water vapour will be condensed out and the nearly pure gas at a pressure of 8 bar can be compressed to a desired shipment pressure for transport of CO₂ in pipeline.

Example 7

The example concerns one or more membrane units where the CO₂-rich gas can have a pressure approximately equal to the partial pressure of CO₂ into the separation unit, as shown in Table 1 below.

Total inlet pressure on the separation unit (bar)	Partial pressure of CO ₂ out from the separation unit (bar)
200	40
250	50
300	60

Claims

1. Method for production of a CO₂-rich gas stream and a H₂-rich gas stream,
c h a r a c t e r i z e d i n that the method comprises the following steps:
- 5 a) natural gas and water are fed to a reforming reaktor and converted to synthesis gas
under supply of a O₂-containing gass;
- b) the gas stream from a) is shifted, whereby the content of CO is reduced and the
amounts of CO₂ and H₂ are increased by reaction of H₂O;
- c) the gas stream from b) is separated in a separation unit into a CO₂-rich and a H₂-
10 rich gas stream, respectively.
2. Method according to claim 1,
c h a r a c t e r i z e d i n that the shift process in b) is carried out in one step.
- 15 3. Method according to claims 1-2,
c h a r a c t e r i z e d i n that the ratio H₂O:CO in the shift process is from 1 to 9.
4. Method according to claims 1-3,
c h a r a c t e r i z e d i n that the ratio H₂O:CO in the shift process preferably is from
20 1.5 to 4.
5. Method according to claims 1-4,
c h a r a c t e r i z e d i n that the pressure in the CO₂-rich gas stream after the separation
unit is from 1 to 100 bar.
- 25 6. Method according to claims 1-5,
c h a r a c t e r i z e d i n that the pressure in the CO₂-rich gas stream after the separation
unit is from 5 to 50 bar.
- 30 7. Method according to claims 1-6,
c h a r a c t e r i z e d i n that the carbon part in the H₂-rich gas stream is from 1 to 20 %
by volume.

8. Method according to claims 1-7,
characterized in that the carbon part in the H₂-rich gas stream is from 5 to 15 %
by volume.
- 5 9. Method according to claims 1-8,
characterized in that the natural gas in step a) is supplied with an oxygen rich
gas.
- 10 10. Method according to claims 1-8,
characterized in that the natural gas in step a) is supplied with air/oxygen en-
riched air.
- 15 11. Method according to claims 1-8,
characterized in that the reformer reactor preferably is a partial oxidation reac-
tor.
- 20 12. Method according to claims 1-11,
characterized in that the reformer reactor particularly is an autothermal refor-
mer.
13. Method according to claim 12,
characterized in that the gas stream from a combustion chamber in an
autothermal reformer is contacted with a catalyst bed.
- 25 14. Method according to claim 11,
characterized in that the reforming is carried out without a catalyst.
- 30 15. Method according to claims 1-14,
characterized in that the gas stream out of the reformer has a temperature wit-
hin the interval from 800 to 1200°C.

16. Method according to claim 10,
characterized in that at least a part of N_2 follows the CO_2 -rich gas stream.

17. Use of a CO_2 -rich gas stream produced according to claim 1 for injection into ma-
5 rine formations.

18. Use of a H_2 -rich gas stream produced according to claim 1 for hydrogenation.

19. Use of a H_2 -rich gas stream produced according to claim 1 as a source of energy /
10 fuel in fuel cells.

20. Use of a H_2 -rich gas stream produced according to claim 1 for the production of
electricity.

1/2

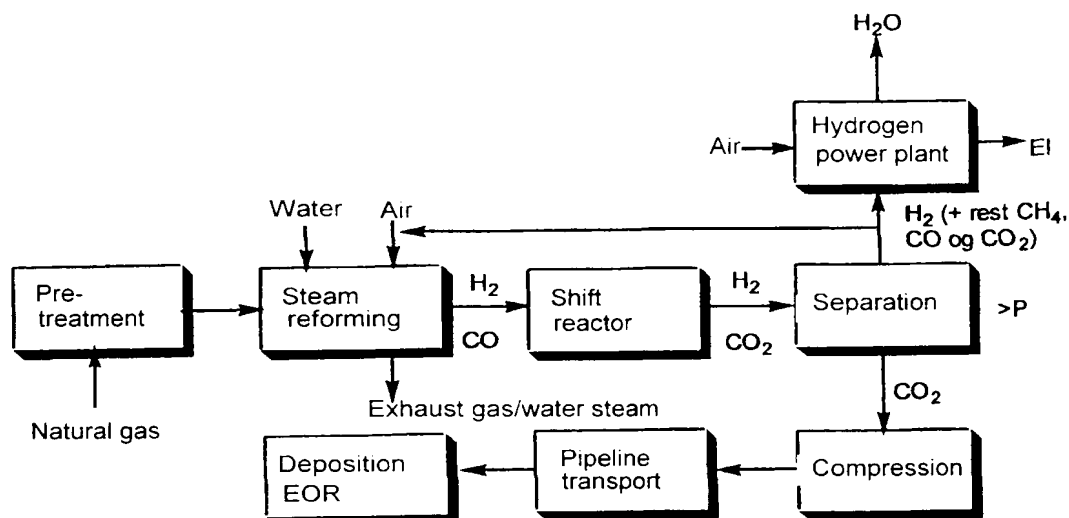


Figure 1 shows known technique in the form of steam reforming with hydrogen firing

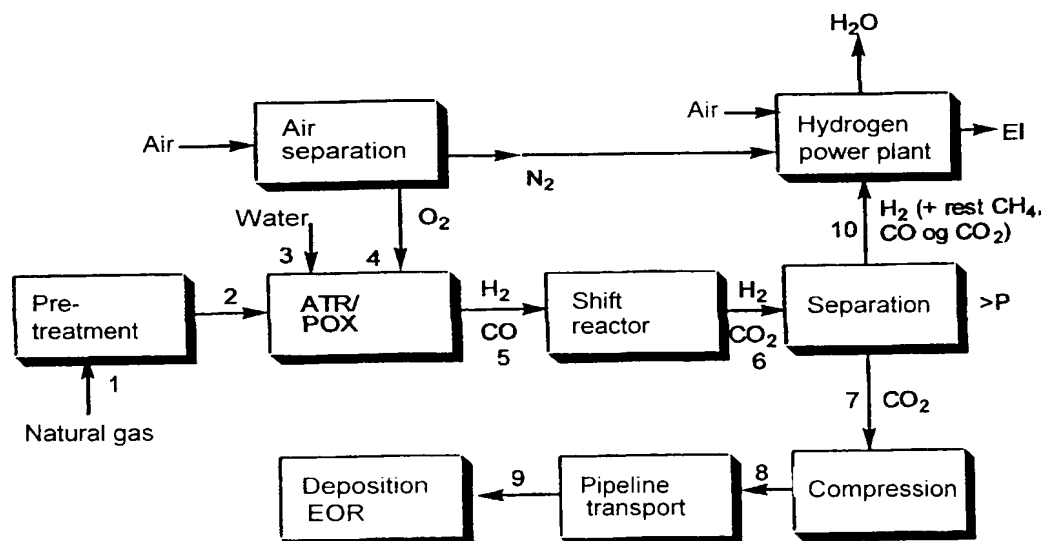


Figure 2 shows POX or ATR with oxygen

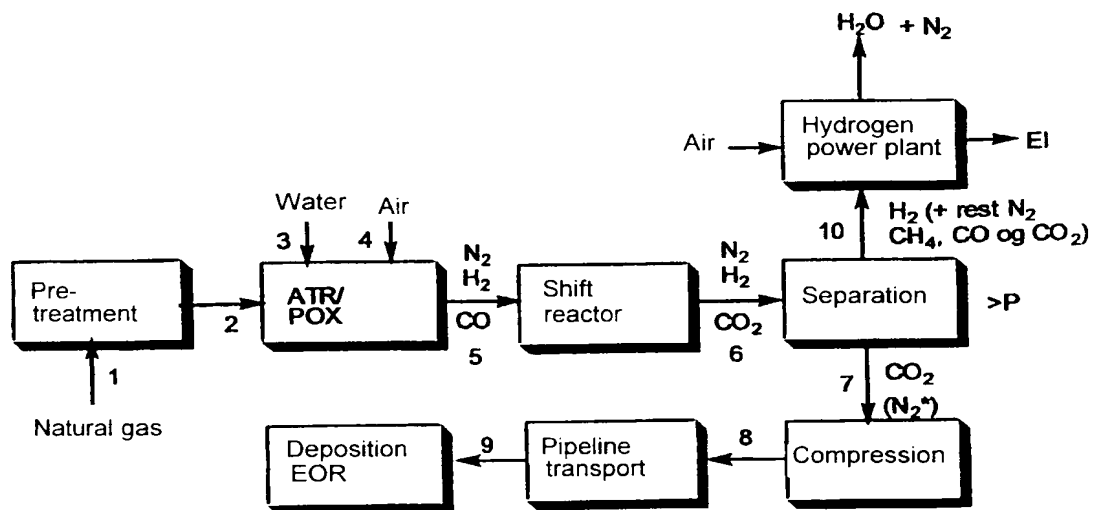


Figure 3 shows POX or ATR with air

(N_2^*): By use of one or more membrane units
 N_2 is run together with CO_2 .

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 99/00280

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C01B 3/32, C01B 31/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

FULLTEXT, EPODOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0289419 A1 (COMPAGNIE FRANCAISE D'ETUDES ET DE CONSTRUCTION"TECHNIP"), 2 November 1988 (02.11.88), column 1, line 15 - line 40; column 2, line 16 - line 38; column 3, line 4 - line 13, column 4, line 48 - line 51; column 4, line 63 - column 5, line 4; abstract --	1-16
X	US 5714132 A (AKHILESH KAPOOR ET AL), 3 February 1998 (03.02.98), column 2, line 39 - line 45; column 5, line 22 - line 26; column 7, line 50 - column 8, line 18, figures 1,3, example II, Table II --	1-16

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

10 March 2000

Name and mailing address of the ISA:

Swedish Patent Office
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Date of mailing of the international search report

14 -03- 2000

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 99/00280

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4699772 A (HANS C. DE LATHOUDER), 13 October 1987 (13.10.87), column 1, line 55 - line 64; column 2, line 6 - line 54; column 3, line 8 - line 9, abstract	1-2,5-6, 9-11,15-16
A	--	3-4,7-8, 12-14
A	US 4681745 A (ALWYN PINTO), 21 July 1987 (21.07.87), column 1, line 11 - line 21, Table 1 & 2	1-16
A	CA 868821 A (GIORGIO PAGANI), 20 April 1971 (20.04.71), column 3, line 20 - line 25; column 4, line 11 - line 22	1-16

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO99/00280

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See extra sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: **1-16**

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO99/00280

- I. Claims 1-16 relate to a process for producing a CO₂- and a H₂-rich gas.
- II. Claim 17 relates to the use of a CO₂-rich gas for injection in marine formations.
- III. Claim 18 relates to the use of a H₂-rich gas for hydrogenation.
- IV. Claim 19 relates to the use of a H₂-rich gas as a source of energy in a fuel cell.
- V. Claim 20 relates to the use of a H₂-rich gas for electricity production.

The special technical feature of Group I is a process for producing the gases H₂ and CO₂. The special technical features of Group II-V involve different applications of the gases H₂ and CO₂. The gases H₂ and CO₂, produced according to claim 1, are well known products. There is a reference in each of the independent claims 17-20 to the process for producing these known products. However, the production process does not give the products any new characteristics, therefore the reference made in claim 17-20 does not involve the features in claim 1. The group of inventions is not so linked as to form a single inventive concept under PCT Rule 13.

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/12/99

International application No.

PCT/NO 99/00280

Patent document cited in search report			Publication date	Patent family member(s)	Publication date
EP	0289419	A1	02/11/88	FR 2614612 A,B	04/11/88
US	5714132	A	03/02/98	EP 0643013 A ZA 9405891 A	15/03/95 13/06/95
US	4699772	A	13/10/87	BR 8600140 A EP 0214991 A JP 61502678 T NL 8402090 A WO 8600286 A FI 865352 A NO 860736 A NL 8402091 A	01/09/87 25/03/87 20/11/86 16/01/86 16/01/86 30/12/86 27/02/86 16/01/86
US	4681745	A	21/07/87	AU 564149 B AU 1328183 A CA 1210222 A EP 0093502 A,B IN 159188 A JP 1778061 C JP 4059249 B JP 58190821 A NZ 203799 A ZA 8302524 A	06/08/87 20/10/83 26/08/86 09/11/83 04/04/87 28/07/93 21/09/92 07/11/83 13/12/85 25/01/84
CA	868821	A	20/04/71	NONE	